

HEYMANN

# PATENT SPECIFICATION

(11) 1284 766

1284 766

NO DRAWINGS

- (21) Application No. 36560/69 (22) Filed 21 July 1969  
(23) Complete Specification filed 25 June 1970  
(45) Complete Specification published 9 Aug. 1972  
(51) International Classification C08J 1/14 C08F 47/08  
(52) Index at acceptance

C3C 1B2 2  
B5A 1G10 1R100 1R14B 1R14C1C 1R14C1X 1R20 1R22X  
1U2AX 2A2 2A3 2A4X 9  
C3P 7A 7D2A1 7F2

(72) Inventors JOHN GERALD McCOY and  
WILLIAM REES FOSTER



## (54) SHAPING FOAMED THERMOPLASTIC RESIN SHEETS

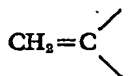
(71) We, MONSANTO CHEMICALS LIMITED, a British Company, of Monsanto House, 10-18 Victoria Street, London, S.W.1., do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—  
This invention relates to a process of shaping thermoplastic resin sheet, and particularly to a process of shaping extruded foamed thermoplastic resin sheet.  
Foamed resins have won wide acceptance in such applications as insulation and packaging where the virtues of resilience, low heat conductivity, lightness and moderate rigidity are particularly prized. Especially prominent among the foamed resins that have been used are the foamed vinylaromatic polymers, particularly foamed polystyrene. Foamed resins can be extruded but it has not proved easy to shape an extruded sheet of such a material, particularly where the density has been in the medium or low range, for instance less than ten pounds per cubic foot, and the thickness has been greater than about one quarter of an inch. In particular, attempts to vacuum-form foamed polystyrene sheets have given products having a strong tendency to warp after a few days, for it is difficult to ensure even heating of the sheets because of their very low thermal conductivity. Furthermore, it is mechanically difficult to arrange the vacuum-forming of foamed resin sheets "in line", that is to say shortly after they have issued from the extruder die, although such in-line operations would be very desirable in that intermediate handling operations would thereby be eliminated. A process has now been devised by which these difficulties can be overcome by shaping the extruded foamed sheet while its interior is still plastic, that is to say before it has reached the point at which

it can not be moulded without application of heat, from the extrusion process.

The process of the present invention is one for the production of a shaped foamed thermoplastic resin sheet, which comprises extruding a sheet of a foamed thermoplastic resin, maintaining the freshly extruded sheet under cooling conditions until a solidified surface skin covers the still-plastic interior of the sheet and, before the interior has solidified, heating the surface skin to render it plastic and applying shaping means to the sheet.

By the interior of the sheet is meant that portion which is furthest removed from the major surfaces of the sheet and which represents at least 60% of the thickness of the sheet.

The extruded foamed resin is preferably a thermoplastic homopolymer or copolymer of a monomeric compound containing the grouping



such as an olefin, for example ethylene or propylene; a vinyl halide or ester for example vinyl chloride or vinylacetate; an acrylic acid derivative such as methyl methacrylate, ethyl acrylate, or acrylonitrile; or a vinyl aromatic compound for example styrene,  $\alpha$ -methylstyrene or ortho-chlorostyrene.

A preferred resin is a homopolymer or copolymer of a vinylaromatic monomer such as for example, styrene,  $\alpha$ -chlorostyrene, vinyltoluene or  $\alpha$ -methylstyrene. A copolymer can be one of a vinylaromatic monomer with another olefinic monomer, for example acrylonitrile, vinyl chloride, vinyl acetate, methyl acrylate, methyl methacrylate, ethyl acrylate, butadiene or isoprene. Toughened polystyrene

45

50

55

60

65

70

75

80

can be employed, for instance one that has been obtained by modification before or after polymerisation with a natural or synthetic rubber. Excellent results have been obtained using polystyrene and this is the most preferred resin. Other preferred resins are a styrene/acrylonitrile copolymer (SAN), or an acrylonitrile/butadiene/styrene (ABS) resin.

The foamed resin sheet is an extruded one, which means that the resin fed to the extrusion die contains a blowing agent. This can be a chemical blowing agent, that is to say a substance, such as for example sodium bicarbonate, ammonium bicarbonate, azodicarbonamide, dinitrosopentamethylene diamine or barium azodicarboxylate, that decomposes to give a gas under the conditions of temperature and pressure within the extruder, but the preferred blowing agent is a volatile substance. In many instances a volatile blowing agent is one that is a gas or vapour under normal atmospheric conditions (such as 20°C and 1 atmosphere pressure), but which while under pressure before extrusion is present in solution in the molten or semi-molten thermoplastic resin. The blowing agent can, however, be one, such as pentane or a pentane fraction, which is a liquid under normal conditions. Examples of volatile substances that can be used include lower aliphatic hydrocarbons such as methane, ethane, ethylene, propane, a butane, a butylene, or a pentane; lower alkyl halides such as methyl chloride, trichloromethane or 1,2-dichlorotetrafluoroethane; acetone, and inorganic gases such as carbon dioxide or nitrogen. An important property of a volatile blowing agent, for the purpose of the present invention, is the rate at which it can permeate out of the freshly extruded foamed sheet; this will be explained below. For the most preferred foamed polystyrene sheet having a density of 1 to 5 pounds per cubic foot the preferred blowing agent is methyl chloride. From 3 to 30 per cent, especially from 5 to 20 per cent by weight based on the weight of the resin is often a suitable proportion of a volatile blowing agent, and for example there can conveniently be used from 7 to 10 per cent by weight of methyl chloride in conjunction with polystyrene. When a permanent gas such as nitrogen, or a chemical blowing agent, is employed much smaller quantities can be employed, such as for example 0.2 to 1 per cent by weight.

The blowing agent can be mixed with the resin in several ways; for example particles of the resin can be dusted with the blowing agent where this is a solid, or steeped in it if it is a liquid, before being fed to the extruder. A preferred method where the blowing agent is a volatile substance and the extruder is of the screw type is to inject the blowing agent under pressure into the extruder barrel.

Where the foamed resin is flammable, there can be incorporated therein a flame-retardant additive, particularly where the resin is a foamed homopolymer or copolymer of a hydrocarbon monomer such as styrene. Other additives, such as for example colourants, antioxidants or plasticisers, can also be included.

The resin can be extruded from any suitable die producing a substantially flat coherent polymer sheet, preferably of uniform thickness. Examples of extruder dies that can be used to produce sheet appropriate for the practice of the present invention are described in British Patent Specifications Nos. 1,034,120, 1,084,000, 1,089,562, 1,098,408, 1,159,920, 1,166,937 and 1,195,279.

The most preferred foamed sheet used in the process of the invention is, however, one in which the cells are elongated in a direction perpendicular to the surface skin such as are described for example in British Patent Specifications 1,089,562 and 1,195,279.

The foamed sheet preferably has a thickness up to 1.25 inch, for example from 0.1 to 1 inch and most preferably from 0.2 to 0.8 inch, and while its density can be chosen from a wide range extending almost up to that of solid unfoamed resin it is preferably not more than 35 pounds per cubic foot and very often much less than this, for instance from 1 to 10, for example from 2 to 4 and especially from 2 to 3 pounds per cubic foot.

In the process of the invention, the freshly extruded sheet is maintained under cooling conditions, for instance a cooling atmosphere, until a solidified surface skin covers the still-plastic interior. Normally a skin forms on each of the major surfaces of the sheet, and the rigidity of the skins is preferably such that the sheet as a whole is self-supporting. The cooling conditions can, for example, comprise a water spray or a pair of cooled platens or rollers, but preferably the sheet is cooled by exposure to a cooling atmosphere. This is preferably air at room temperature and pressure, and it can be blown on to the sheet if desired. The atmosphere can have a temperature above or below room temperature, provided that it produces the solidified surface skin. Skin formation does, of course, take place as a result of cooling of the surface, for example, by radiation and convection, but when the blowing agent employed is a volatile one there is another way in which skin formation is assisted. A volatile blowing agent often has a plasticising action, that is to say it reduces the heat-distortion temperature of the resin, and thus when a freshly extruded sheet of a foamed resin containing a volatile blowing agent is exposed to the atmosphere and the blowing agent is in consequence lost by permeation from the exposed surface of the sheet, a solidified surface skin is soon

formed while the sheet interior remains plastic.

Preferably a skin representing up to 20% of the thickness of the sheet is allowed to form on each major surface of the sheet. More preferably, however, the thickness of each such a skin represents from 2.5% to 15%, and most preferably from 5% to 10% of the total thickness of the sheet. Normally the skins on the two major surfaces are of equal thickness but this is not essential.

The time during which the sheet can be allowed to cool whilst still retaining the plasticity of the interior depends on the thickness of the sheet, the ambient conditions, the density of the foam and on the rate at which the blowing agent permeates out from the foam structure. This last factor can be of considerable practical importance in view of the plasticising action of the blowing agent on the resin as stated above. By an appropriate choice of blowing agent it is possible either to minimise the effect of this plasticising action or to utilise it, according to practical working conditions. For example, where (as is preferred) the shaping means is located relatively near to the extruder die and it is desired to pass the extruded foamed sheet to the shaping means with only a short intervening cooling period, it would be appropriate to choose a blowing agent having a relatively high permeation rate so that the cooling time would be only a few minutes or even less. In this way can be achieved the advantages of "in-line" operation. On the other hand, some flexibility of operation can be achieved by choosing a more slowly-permeating blowing agent so that the cooling time can be longer, for example up to several hours, so that a working stock of unshaped foamed resin sheets can be held in order to absorb any small variations in the speed of the extruder or the shaping means. In general the time during which the foamed sheet can be allowed to cool can be as little as 5 minutes or less, or as long as 12 hours or more, depending on the blowing agent permeation rate. Examples of rapidly-permeating blowing agents are methyl chloride or a mixture of methyl chloride and methylene dichloride, whereas dichlorodifluoromethane is relatively slow. The rate at which any particular blowing agent permeates away is best found by experiment under actual operating conditions. The blowing agent can be a mixture of compounds so as to give the required rate of solidification to the sheet interior.

It is therefore not possible to give a definite rule for the length of the cooling time. For example, however, it has been found that if a foamed polystyrene sheet is  $\frac{1}{2}$  inch in thickness and has been foamed using a methyl chloride-blowing agent to give a foam having a density of from 2 to 3 pounds per cubic foot, it can be left in air at room temperature

for up to 2 hours such as for example from 5 minutes to  $1\frac{1}{2}$  hours before the interior portion is no longer plastic. In practice, with a sheet of the above description the cooling time is conveniently from 5 to 60 minutes, preferably from 10 to 30 minutes, for example about 10 minutes.

The heat applied to the surface skin to render it plastic before the application of the shaping means is normally applied to each major surface of the sheet, preferably to both, at the same time. It can be accomplished by any convenient means such as, for example, a radiant heating panel, an infra red lamp, an electric strip heater or a ceramic radiator with embedded heating elements. A radiant heater supplying heat to the surface of the polymer sheet at a rate of from 0.05 to 1 watt per square centimetre, preferably from 0.1 to 0.85 such as for example from 0.25 to 0.50 watt per square centimetre, is normally suitable.

The heating is continued until the surface skins of the foamed resin sheet are sufficiently plastic to allow the sheet to be shaped. The degree of heating is preferably sufficient to raise the temperature of the surface skin to from 3 to 20°C such as from 5 to 15°C above the heat distortion temperature of the foamed resin (allowance being made for any residual volatile blowing agent that might still be present in the resin of the skin). Very satisfactory results have been obtained by heating the surface skin to from 7 to 10°C above the heat distortion temperature of the foamed resin. The heating time will depend on the intensity of the heating employed and the thickness and density of the foam sheet, and is thus best found by experiment. In general, a heating time between 5 seconds and 5 minutes is usually sufficient, preferably between 10 seconds and 3 minutes.

The shaping means employed can for instance be any conventional fluid-pressure forming means, matched dies, or a combination of two or more of these methods, for example the shaping can be accomplished by the use of male and female moulds assisted by evacuation of the female mould during the shaping process.

Fluid-pressure forming is a process in which a heat softened sheet is forced by means of a differential fluid-pressure into conformity with a mould and is then allowed to cool until it is set in the shape of the mould. Usually the mould is cooled, for instance by water.

A fluid-pressure forming process can be the process known as vacuum forming where the differential fluid-pressure is achieved by reducing the air pressure on the same side of the sheet as the mould, or a pressure-forming process where a compressed gas (usually air) is applied to the other side of the sheet;

alternatively a combination of both methods can be employed.

Where a fluid-pressure forming process is employed the length of time that the sheet is held in contact with the mould depends on the thickness and density of the sheet as well as the mould temperature, but normally does not exceed 1 minute, and is often from 1 second to 30 seconds. Thus, by way of illustration, a sheet of density 2 to 3 pounds per cubic foot and thickness  $\frac{1}{2}$  inch normally requires from 2 to 20 seconds. The pressure employed in a fluid-pressure forming process should, of course, not be so great as to cause collapse of the foam. About 3 to 10 pounds per square inch is often satisfactory.

Other examples of shaping means that are suitable for the process of this invention comprise matching male and female mould dies or mating rollers (preferably cooled) having an appropriate profile, such as for example a corrugated profile.

The process of the invention is particularly useful for the production of shaped articles, such as for example packaging or other containers, in which moderate rigidity combined with lightness is required. Other shaped articles which can very conveniently be made by the process include corrugated or other shaped sheets of foamed vinylaromatic polymers, such as are useful in the production of heat- and sound-insulating building panels, and in laminates such as are described in British Patent Specification No. 1,248,627.

The invention is illustrated by the following Examples.

#### EXAMPLE 1

This Example describes a process, according to the invention, for shaping an extruded foamed polystyrene sheet.

An extruded foamed polystyrene sheet 16 inches wide and  $\frac{5}{8}$  inch thick and of density 2.3 pounds per cubic foot made using 7.5% by weight of methyl chloride as blowing agent was allowed to cool in air at 17°C until approximately 5 minutes after leaving the extrusion die. At this time a solidification skin of thickness about 0.1 inch had formed on each major surface of the sheet, whilst the sheet interior remained plastic. The sheet was then passed between a pair of electric radiant heaters supplying heat at an intensity of 0.25 watts per square centimetre to the top and bottom surfaces of the sheet. After a residence time of 36 seconds between the heaters the surface skins had become plastic again and the sheet was then passed between a mating pair of corrugated water-cooled rollers. A rigid corrugated foamed polystyrene sheet was obtained.

#### EXAMPLE 2

This Example describes a process, accord-

ing to the invention, for vacuum-forming foamed polystyrene sheet.

A number of extruded foamed polystyrene sheets of thickness  $\frac{1}{2}$  inch and densities ranging between 2 and 3 pounds per cubic foot, and made using about 7.5% by weight of methyl chloride as blowing agent, were allowed to cool in air at 17°C for 5 minutes after leaving the extrusion die. The top and bottom surfaces of each sheet were heated for 0.5 minutes with electric radiant heaters supplying heat at an intensity of 0.25 watts per square centimetre to the surface. They were then vacuum formed into seed trays of dimensions  $15\frac{1}{2}$  inches  $\times$   $9\frac{3}{4}$  inches  $\times$  2 inches and wall thickness of  $\frac{1}{8}$  inch. Heating times used were in the range of 45 to 60 seconds, and the mould dwell times were 10 seconds in each case.

#### WHAT WE CLAIM IS:—

1. A process for the production of a shaped foamed thermoplastic resin sheet, which comprises extruding a sheet of a foamed thermoplastic resin, maintaining the freshly extruded sheet under cooling conditions until a solidified surface skin covers the still-plastic interior of the sheet and, before the interior has solidified, heating the surface skin to render it plastic and applying shaping means to the sheet.

2. A process according to Claim 1, in which the resin is a thermoplastic homopolymer or copolymer of a vinylaromatic monomer.

3. A process according to Claim 2, in which the resin is polystyrene.

4. A process according to any of the preceding claims, in which the foamed thermoplastic resin sheet is produced by feeding to an extrusion die a foamable thermoplastic resin containing a blowing agent that is a volatile substance as herein defined.

5. A process according to Claim 4, in which the blowing agent comprises methyl chloride.

6. A process according to either of Claims 4 and 5, in which the amount of blowing agent is from 5 to 20% by weight based on the weight of resin.

7. A process according to any of the preceding claims, in which the foamed sheet has a thickness from 0.1 to 1 inch.

8. A process according to any of the preceding claims, in which the density of the foamed sheet is from 1 to 10 pounds per cubic foot.

9. A process according to any of the preceding claims, in which a skin is formed on each of the major surfaces of the sheet, the rigidity of the skins being such that the sheet as a whole is self supporting.

10. A process according to any of the preceding claims, in which a skin representing from 2.5% to 15% of the thickness of

the sheet is allowed to form on each major surface of the sheet.

- 5 11. A process according to any of the preceding claims, in which the surface skin is heated by means of a radiant heater.

- 10 12. A process according to Claim 11, in which the heater supplies heat to the surface of the foamed thermoplastic resin sheet at a rate from 0.1 to 0.85 watt per square centimetre.

- 15 13. A process according to any of the preceding claims, in which the degree of heating is sufficient to raise the temperature of the surface skin by from 7 to 10°C. above the heat distortion temperature of the foamed resin.

- 20 14. A process according to any of the preceding claims, in which the shaping means comprises a fluid pressure forming means.

15. A process according to any of the

preceding claims, in which the shaping means comprises matched dies.

16. A process according to any of the preceding claims, in which there is produced a corrugated sheet.

- 25 17. A process according to any of Claims 1 to 15, in which there is produced a packaging container.

- 30 18. A process for the production of a shaped foamed resin sheet substantially as described in either of the Examples.

19. A shaped foamed resin sheet that has been produced by a process according to any of the preceding claims.

C. G. WICKHAM,  
Chartered Patent Agent,  
Monsanto House,  
10—18, Victoria Street,  
London, S.W.1.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1972.  
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.